NOVONIX
BATTERY TECHNOLOGY SOLUTIONS

Estimating measurement error in Coulombic Efficiency with UHPC

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1. Introduction

NOVONIX's UHPC Channel Modules are capable of making measurements of current with precisions of better than 20 parts per million across their measurement ranges. But how does that precision in current translate to precision in measurements of CE? This paper will explore how we estimate our measurement error in CE from our raw data.

2. Initial approach

2.1 Theory

Coulombic Efficiency, CE, is given by:

$$CE = \frac{I_c t_c}{I_d t_d} \tag{1}$$

where I_c and t_c are charge current and charge time respectively, with I_d and t_d are discharge current and discharge time.

If we let $CE = f(I_c, t_c, I_d, t_d)$, then:

$$\delta f = \sqrt{\left(\frac{\partial f}{\partial I_c}\delta I_c\right)^2 + \left(\frac{\partial f}{\partial t_c}\delta t_c\right)^2 + \left(\frac{\partial f}{\partial I_d}\delta I_d\right)^2 + \left(\frac{\partial f}{\partial t_d}\delta t_d\right)^2} \tag{2}$$

and the error in CE is given by:

$$\Delta CE = \sqrt{\left(\frac{t_c}{I_d t_d}\Delta I_c\right)^2 + \left(\frac{I_c}{I_d t_d}\Delta t_c\right)^2 + \left(-\frac{I_c t_c}{I_d^2 t_d}\Delta I_d\right)^2 + \left(-\frac{I_c t_c}{I_d t_d^2}\Delta t_d\right)^2} \tag{3}$$

2.2 Results

Now we'll calculate ΔCE precision for a specific experiment. We can take the following case, where a cell has been charged and discharged with a 200mA CC charge over an hour each way (a perfect CE of 1).

NOVONIX UHPC Channel Modules can deliver a current resolution better than 20ppm FSR, and have a timing resolution of 10ms. So, our parameters become:

Parameter	Value	Resolution
I_c	200mA	8×10^{-6} A*
t_c	3600s	0.01s
I_d	200mA	8×10^{-6} A*
t_d	3600s	0.01s

*based on a 2A Channel Module with an FSR of 0.02%

Using the expression derived for ΔCE, we find $\Delta CE = 6 \times 10^{-5}$ or 60ppm.

HOWEVER. There is a flaw in this approach: it only works in an idealized scenario, where there is a single measurement of I_c and a single measurement of t_c. Real cycling experiments are not like this; they consist of many measurements taken over a long period of time. We need a refined approach.

3. Refining the approach

3.1 Theory

Let's take our original expression for CE, i.e.

$$CE = \frac{I_c t_c}{I_d t_d}$$

and rewrite it as:

$$CE = \frac{f}{g} \tag{4}$$

Therefore, the error in CE, δCE is given by:

$$\delta CE = \sqrt{(\frac{\partial CE}{\partial f}\delta f)^2 + (\frac{\partial CE}{\partial g}\delta f)^2} \tag{5}$$

Which becomes:

$$\delta CE = \sqrt{(\frac{\delta f}{g})^2 + (-\frac{f\delta g}{g^2})^2} \tag{6}$$

$$\Delta CE = \sqrt{(\frac{\Delta f}{g})^2 + (-\frac{f\Delta g}{g^2})^2} \tag{7}$$

Now, since f and g are *actually* discrete sums, automatically calculated by our UHPC devices as the total of all the current $\times$ time steps for a charge or discharge step, it's truer to write f and g as:

$$f = \sum^{i} {}^{i}\mathbf{I_c}{}^{i}\mathbf{t_c}$$

$$g = \sum^{j} {}^{j}\mathbf{I_d}{}^{j}\mathbf{t_d} \tag{8}$$

If we expand f for the first few terms, you can start to see how we get Δf and Δg, which we'll ultimately need to get our estimate of ΔCE in (7):

$$f = \sum^{i} {}^{i}\mathbf{I_c}{}^{i}\mathbf{t_c} = {}^{1}\mathbf{I_c}{}^{1}\mathbf{t_c} + {}^{2}\mathbf{I_c}{}^{2}\mathbf{t_c} \ldots$$

$$\delta f = \sqrt{(\frac{\partial f}{\partial^1 \mathbf{I_c}}\delta^1\mathbf{I_c})^2 + (\frac{\partial f}{\partial^1 \mathbf{t_c}}\delta^1\mathbf{t_c})^2 + (\frac{\partial f}{\partial^2 \mathbf{I_c}}\delta^2\mathbf{I_c})^2 + (\frac{\partial f}{\partial^2 \mathbf{t_c}}\delta^2\mathbf{t_c})^2 \dots} \tag{9}$$

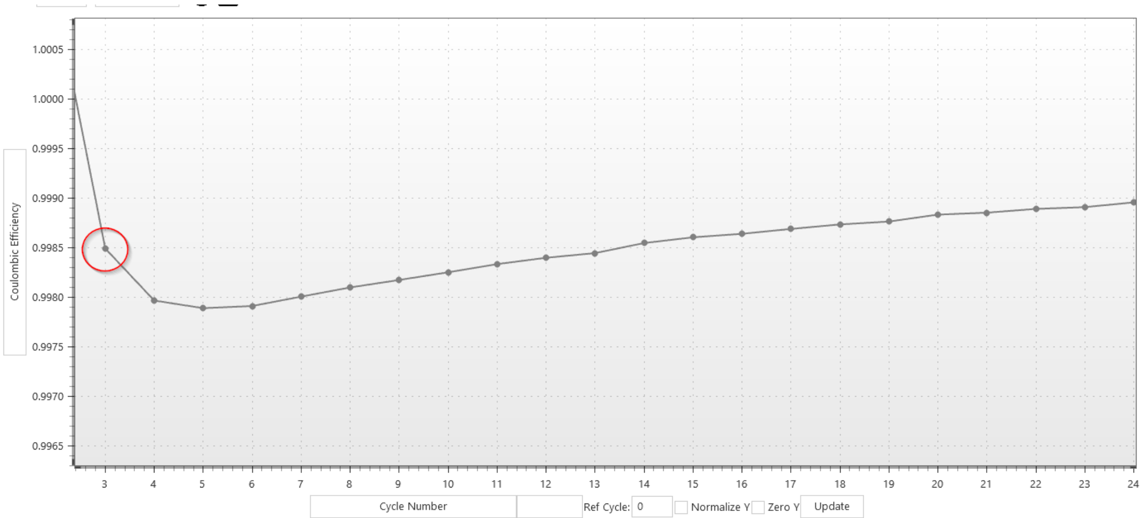
$$\Delta f = \sqrt{(\Delta^1\mathbf{I_c}{}^1\mathbf{t_c})^2 + (\Delta^1\mathbf{t_c}{}^1\mathbf{I_c})^2 + (\Delta^2\mathbf{I_c}{}^2\mathbf{t_c})^2 + (\Delta^2\mathbf{t_c}{}^2\mathbf{I_c})^2 \dots}$$

$$\therefore \Delta g = \sqrt{(\Delta^1\mathbf{I_d}{}^1\mathbf{t_d})^2 + (\Delta^1\mathbf{t_d}{}^1\mathbf{I_d})^2 + (\Delta^2\mathbf{I_d}{}^2\mathbf{t_d})^2 + (\Delta^2\mathbf{t_d}{}^2\mathbf{I_d})^2 \dots} \tag{10}$$

All that's left to do is gather some data and calculate a value for ΔCE.

3.2 Results

We can use the sample data available for download in the Customer Area on the NOVONIX Website. From Novonix_Sample_Data_1_NMC811_graphite_25V-42V_40C_C10-C10_1 csv, we'll extract Cycle 3.



Parameter	Value	Resolution (Δ)
${}^i\mathbf{I_c}$	286 values, Novonix_Sample_Data_1	8×10^{-6} A*
${}^i\mathbf{t_c}$	286 values, Novonix_Sample_Data_1	0.01s
${}^j\mathbf{I_d}$	285 values, Novonix_Sample_Data_1	8×10^{-6} A*
${}^j\mathbf{t_d}$	285 values, Novonix_Sample_Data_1	0.01s

*based on the 2A Channel Module specification, 200mA range (FSR of 0.02%)

Using the sample data with the associated precision estimates of our ability to measure current and time, we get the following results:

Parameter	Value	Units	Notes
f	1183.8272	C	Equation (8)
Δf	0.0226	C	Equation (10)
g	1186.2373	C	Equation (8)
Δg	0.0221	C	Equation (10)
CE	0.997968	-	Equation (4)
ΔCE	0.000027	-	Equation (7)

CE, **precise to within 27ppm**.

Hint

Be sure to use the right numbers. The measurement error in Coulombic Efficiency is highly experiment-dependent.

For example, imagine a protocol that uses a 150mA charge, but a 5mA discharge. On a UHPC 2A Channel Module, the 20ppm FSR resolution for the charge step is based on a 200mA range, while the discharge step is based on a 20mA range - an order of magnitude higher res.

Be sure to account for these and other factors when gathering your data.

Idea

Try working through this application note to estimate the error in *accuracy* in one of your CE measurements. Be sure to use the appropriate measurement error specifications from the datasheet appropriate for your equipment.

4. A note on 'Capacity Overshoot'

In any charge or discharge step, there is always some overshoot; the cut-off voltage must be exceeded in order for the control software to end the step. This effect can skew our calculation of CE.

NOVONIX's UHPC Control Software accounts for this by monitoring the cycle until the cut-off Voltage is exceeded, then interpolates between the ultimate and penultimate point to ensure that in our CE calculation, the overshot voltage point is not used. The theoretical contribution of error from this effect is difficult to estimate; the amount of overshoot largely depends on the charge rate of the step, the length of charge time and the linearity of current at that point, but it is safe to say this is a relatively minor point in the grander scheme of calculating CE for an entire charge cycle.